

Evidence of bad recycling practices

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DOI:

[10.1039/c7em00160f](https://doi.org/10.1039/c7em00160f)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Guzzonato, A, Puype, F & Harrad, SJ 2017, 'Evidence of bad recycling practices: BFRs in children's toys and food-contact articles', *Environmental Science Processes and Impacts* . <https://doi.org/10.1039/c7em00160f>

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Environmental Science Processes & Impacts

ARTICLE

Evidence of Bad Recycling Practices: BFRs in Children's Toys and Food-Contact Articles

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Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Brominated flame retardants (BFRs) have been used intentionally in a wide range of plastics, but are now found in an even wider range of such materials (including children's toys and food contact articles) as a result of recycling practices that mix BFR-containing waste plastics with "virgin" material. In this study Br was quantified in toy and food contact samples on the assumption that its concentration can be used as metric for BFR contamination. Subsequently, compound specific determination of BFRs was performed to evaluate the validity of the aforementioned assumption, crucial to render rapid, inexpensive, in-situ Br determination in non-laboratory environments (such as waste handling facilities) a viable option for sorting waste according to their BFR content. We report semi-quantitative compound specific BFR concentrations to give an overview of the distribution of individual BFRs in the analyzed samples. Finally, we evaluated the correlations between waste electrical and electronic equipment (WEEE) related substances (Ca, Sb and rare earth elements (REEs)) and Br as a proxy for identifying poor sorting practices in different waste streams. 26 samples of toys, food-contact articles and WEEE were analyzed with a suite of different techniques in order to obtain comprehensive information about their elemental and molecular composition. The information obtained from principal component analysis about WEEE-related compounds provides new insights into the influence of sorting practices on the extent of products' contamination and bringing out polymer-related trends in the pollutants' signature. 61% of all samples were Br positive: of these samples, 45 % had decaBDE concentrations exceeding the concentration limits for PBDEs and their main constituent polymer was - according to the REEs signature of such samples - Acrylonitrile Butadiene Styrene (ABS); uses of which include copying equipment, laptops and computers. The ability to better track chemicals of concern and their trends in products is the main requirement for high-level management and control of material-cycles to become non-toxic in the future as proposed in the EU's 7th Environmental Action Plan.

Introduction

As a result of concerns about their environmental impact, some BFRs such as polybrominated diphenyl ethers (PBDEs) have since the mid-2000s, been subject to bans and restrictions on their manufacture and new use within several jurisdictions including the European Union. Such legislative actions do not address their presence in existing items however, and the presence of restricted BFRs in plastic materials reaching the waste stream is now a serious concern. For example, the presence of restricted BFRs in new plastic items at levels not commensurate with flame retardancy, suggests that recycling of FR-treated polymers is leading to contamination of new goods.¹⁻³ A 2015 study⁴ found significant amounts of PBDEs in 43% of 21 inspected children's toys. To address this issue, the European Commission's Restriction of

Hazardous Substances (RoHS) and WEEE directives stipulate that WEEE that contains polybrominated biphenyls (PBBs), PBDEs, and hexabromocyclododecane (HBCDD) at concentrations exceeding 0.1 weight % cannot be recycled. These limit values are referred to as low Persistent Organic Pollutants (POP) concentration limits. In this study, concentrations of Br are measured in plastic children's toys and food-contact articles, as such items are not required to meet fire safety regulations and are of relevance for human exposure.^{5,6} A polymeric food-contact article is described as any polymeric item intended to come in contact with food. Regulations for food-contact articles fall under the European Commission Regulation 10/2011⁷ which only establishes limits for evaluated constituents migrating into food or well defined food-simulating solutions. As for the actual BFR concentration limits in polymers, the guidance prescribes the use of food-grade plastic, to avoid the risk of BFR contaminated plastic coming from recycled material. For toys such regulation is still not in place, therefore sourcing of materials is not restricted to "new/virgin" polymers.⁸ Evidence of restricted BFRs as unintended trace contaminants in new plastic items such as children's toys and food-contact articles has been documented in recent years,⁹ suggesting that the recycling of FR-treated polymers is indeed leading to the contamination of new goods.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Studies into this area remain preliminary in nature, with quantification of unintended trace contaminants in new plastic items not yet carried out on a large-scale, nor has much progress been made into identifying the specific origins of such unintended trace contaminants.

Moreover, the need to verify compliance with low POP concentration limits for BFRs in materials requires a rapid, inexpensive and reliable *in-situ* method that provides a viable alternative to conventional methods based on gas or liquid chromatography interfaced with mass spectrometry. Waste items are initially differentiated in operational categories when entering the waste stream (e.g. large cooling equipment, small WEEE, large WEEE, cathode ray tube monitors, flat screen televisions).¹⁰ The items in these categories contain certain inorganic substances which are characteristic of their destination of use. The practice of mixing recycled plastic in food-contact articles is illegal in Europe; however, as an exemption, re-use of polyethylene terephthalate (PET) is assumed to be safe as the PET cycle is a closed-loop recycling process. This process is described in detail elsewhere¹¹ but in brief it consists of a waste management practice where a certain component (e.g. PET) is meant to be recycled indefinitely through the same waste pathway (e.g. water-bottle waste stream) as long as it can be guaranteed that no other waste stream (e.g. WEEE) is flowing into the closed loop. This is a case where waste-tracking information is used to allow certain materials to be sourced for the production of food-contact articles. We make a case for establishing closed-loop recycling for toys and food-contact articles, and hypothesize a way of verifying that no unintended trace contaminants enter this loop. This concept is in line with the EU's 7th Environmental Action Plan: "Closing the loop"¹² that suggests circular economy strategies to create non-toxic material cycles that facilitate recycling and improve uptake of secondary raw materials. For this reason it is crucial to find a method to:

1. Quantify *in-situ* unintended trace contaminants in individual samples: for this purpose we evaluate the suitability of handheld X-ray fluorescence spectrometers as an inexpensive, rapid, *in-situ* measure of Br and Sb by validating against laser ablation-inductively coupled plasma-mass spectrometry. Once this is verified, we evaluate the suitability of X-ray fluorescence Br measurements as a surrogate indicator of the presence of BFRs in polymers by validating against thermal desorption-GC-MS. This assumption is verified if a Br-positive sample is always also a BFR-positive sample.
2. When samples are BFR-positive, identify their source in the waste stream to stop them from entering the loop again. We evaluate for this purpose the use of information on the inorganic composition of samples, its relationship with the Br content, and the polymeric matrix.

Moreover, as alluded to above, while screening tools like hand-held X-ray fluorescence may provide an acceptable

measure of Br in polymers, they do not provide information on the chemical form of that Br, in particular whether the Br detected arises from a regulated BFR.¹³⁻¹⁵ As Sb₂O₃ is widely used as a co-additive with PBDEs added to flame retardancy¹⁶ but is not used in conjunction with other regulated BFRs, we hypothesise that detection in a given sample of both Br and Sb provides a simple indicator of whether the Br detected arises from the presence of PBDEs. We measured the concentrations of Br, Sb and WEEE related rare earth elements (REEs) in down-stream items (new food-contact articles and toys) that are likely to contain recycled fractions coming from different upper-level waste streams. Principal component analysis was used to correlate REEs (Ca, Y, La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) to the type of polymer they were mixed with, in order to investigate which items (waste category) and through which waste stream the plastic used to produce the analyzed sample was sourced. In summary, the objectives of this study are to add to the currently sparse database on the presence of BFRs as unintended trace contaminants in polymeric consumer goods, by investigating the extent to which food-contact articles and toys currently present on the market contain BFRs at concentrations exceeding low POP concentration limits; to provide new insights into the origins of these unintended trace contaminants; and finally to conduct a preliminary evaluation of our hypothesis that simultaneous detection of both Br and Sb is a reliable indicator of the presence of PBDEs in a given polymer sample.

Materials and methods

Measurement of Br and Sb in samples was conducted using hand-held X-ray fluorescence, with validation against measurements provided by laser ablation-inductively coupled plasma-mass spectrometry.

X-ray fluorescence spectrometry analysis

A Thermo Scientific Niton XL3T Gold Plus handheld device was used, equipped with a geometrically optimised large drift silicon detector and a 50 keV X-ray tube. The analysis was performed with a molybdenum filter, the emission fluorescence line chosen for quantification of Br was K α 1 (11.92 keV) and the relatively less intense K β 1 was used for qualitative evaluation of the spectra (13.29 keV). Proprietary Thermo Scientific NDT software was employed to develop a nine-point calibration for Br and Sb using solid reference materials.

Spectral precision was automatically calculated as two times the SD between each recursive measurement cycle performed during the sampling time. Analytical precision was calculated as the RSD between 4 repeated measurements. For X-ray fluorescence the LOD was calculated as three times the SD of ten replicate blank measurements (bromine free ABS reference material), with the LOQ calculated as 10 times that SD.

Laser ablation-inductively coupled plasma-mass spectrometry analysis for X-ray fluorescence validation and quantification of REEs

Laser ablation-inductively coupled plasma-mass spectrometry was conducted using a Teledyne CETAC Technologies Analyte™ G2 nanosecond excimer laser (ArF) hyphenated to a Thermo Scientific iCAP-Q ICP-MS. The Thermo Scientific Qtegra ISDS software platform was used for laser ablation-inductively coupled plasma-mass spectrometry data acquisition and evaluation. The Chromium software platform was used to control the Analyte G2 LA. For laser ablation-inductively coupled plasma-mass spectrometry the limit of detection was defined as 3 times the standard deviation of signal obtained for the blank (a bromine-free ABS reference material) and the LOQ as 10 times that SD.

Br quantification

A recently developed matrix matched calibration procedure¹⁵ for laser ablation-inductively coupled plasma-mass spectrometry and a thickness correction developed for X-ray fluorescence were applied for the analysis of these samples and compared to the uncorrected laser ablation-inductively coupled plasma-mass spectrometry and X-ray fluorescence measurements.

A calibration for both X-ray fluorescence and laser ablation-inductively coupled plasma-mass spectrometry was performed with nine solid reference materials where known amounts of BDE209 (0%, 0.08%, 0.4%, 0.8%, 1.6%, 2.4%, 5.7%, 8.0% and 12.0% w/w Br; Fig. 1, SI) and Sb in the form of Sb₂O₃ (0%, 0.08%, 0.3%, 0.76%, 1.2%, 1.8%, 2.5%, 3.1%, 3.9% w/w Sb; Fig. 2, SI) where thoroughly homogenized into Br-free ABS. More information on how these reference materials were produced and tested can be found elsewhere.¹⁵

REEs quantification

A glass-based solid reference material NIST 612 and solid reference material NIST 610 containing Y, La, Ce, Pr, Nd, Sm, Gd, Tb, and Dy at concentrations respectively spanning approximately one order of magnitude were used for a two-point calibration. The same data acquisition method used for Br was used for REEs.

Thermal desorption Gas Chromatography-mass spectrometry

For the identification of BFRs, a thermal desorption unit (double-shot Pyrolyser EGA/PY-3030D, Frontier Laboratories LTD., Koriyama, Japan) equipped with a 48-position auto-sampler (Auto-Shot Sampler AS-1020E, Frontier Laboratories LTD., Koriyama, Japan) was used. This was interfaced with a GC-MS (GC-MS QP2010 Plus, Shimadzu, Kyoto, Japan). As for PBDEs and PBBs a short elution time is favoured, a short ultra-alloy separation column was used (Ultra ALLOY-PBDE; 0.25 mm inner diameter x 15 m; 0.05 µm film of dimethyl polysiloxane, Frontier Laboratories LTD., Koriyama, Japan).

For the semi-quantitative evaluation of the relative concentrations of BFRs in the samples, a one-point calibration

was performed using a previously characterised sample (PBDE-treated plastic TV casing sample) (for more details see Table 1 and 2, SI). The obtained calibration slope for each target BFR was used to convert the GC peak intensity into a concentration value. The relative concentration of the single compounds in each sample was normalized against the total concentration of Br to give a representative compound specific concentration profile of each sample. The analytical error was calculated as the SD between two replicate runs for each sample.

The applied ionization mode was electron impact with ionization energy of 70 eV having all peaks monitored by the Fast Automated full Scan - Single ion monitoring Technique which enables acquisition of both full scan and single ion monitoring data on one peak. The Fast Automated full Scan - Single ion monitoring Technique mode for BFR screening in polymers enables to effectively make conclusions concerning the presence of polymeric BFRs (e.g. oligomers from dibromostyrene copolymer), reactive BFRs (e.g. TBBP-A and derivatives) or reaction products from thermal debrominated additive BFRs (e.g. tribromobisphenol A from TBBP-A). This method is designed as a screening method for common BFRs (target analytes) on the market, to identify their appearing degradation products (non-target analytes) and to detect newer BFRs.¹⁷⁻¹⁹

Attenuated total reflection-Fourier transform infrared spectroscopy

For identification of the main polymer matrix, a Shimadzu IRPrestige FTIR spectrophotometer (Kyoto, Japan) equipped by a single reflectance diamond attenuated total reflection crystal was used. All spectra were compared with commercial libraries e.g. RoHS; ATR-Polymer2; IRs Polymer2; T-Polymer2 combined with in-house libraries requiring a minimal match of 90 % or higher.

Pyrolysis GC-MS

Pyrolysis-GC-MS was used as an additional instrumental method that enables a reproducible characterization of (co-)polymers either as a major component or as a trace contaminant. This method detects monomers and significantly abundant pyrolysis degradation products to get a full composition overview of the polymer matrix. The hardware configuration is the same as used for the thermal desorption GC-MS experiment – i.e. the pyrolyzer is programmed at a temperature of 650 °C, injecting up to 10 mg of the isolated sample. All peaks from the pyrograms were identified by using the NIST 05 library (National Institute for standards and Technology, USA). Similar to the thermal desorption GC-MS method, all measurements were repeated twice and compared to blank measurements to check the cleanliness of the system and to avoid potential carry-over issues.

Sampling strategy

In this study we selected samples that are likely relevant to human exposure.

26 polymeric samples were obtained (more than 1 sub-sample was taken from some items) from 16 toys, 9 food-contact articles and one item of WEEE (this was included in the sample list to compare concentration levels and the presence of REEs between different applications.²⁰ The toys and food-contact articles were purchased on the European market: Italy, Czech Republic and Germany; however they were made in China and Turkey (Table 3, SI).

Our samples of food-contact articles and toy materials were not part of an electrical or electronic device (no RoHS restriction) and should not contain BFRs to meet fire safety regulations.

Sample preparation

For hand-held X-ray fluorescence spectrometry and laser ablation-inductively coupled plasma-mass spectrometry measurements, samples were wiped with ethanol, their thickness measured with a digital calliper and then cut into pieces of at least 8 mm diameter.

For thermal desorption-GC-MS and Py-GC-MS the sample preparation method is described in detail elsewhere.¹⁹

Principal Component Analysis

The choice of WEEE-related elements monitored was made by selecting the chemicals that are used in association with BFRs (i.e. Sb_2O_3 , used as a co-synergist in the radical reaction between PBDEs and O_2 as well as CaCO_3 , used mainly as moulding agent,^{21,16} for which a linear correlation with PBDEs is to be expected; REEs were also chosen because of their use in electric components and their otherwise extremely low natural concentrations. Descriptive statistics were applied to study the intra-sample variance between concentrations of Br and REEs between and within different polymeric matrices to highlight influential components responsible for the difference between REEs concentrations in different polymer types. Identification of the polymer matrix was achieved combining attenuated total reflectance Fourier-transformed infrared spectroscopy and pyrolysis-GC-MS.

Results and discussion

X-ray fluorescence spectrometry vs. laser ablation-inductively coupled plasma-mass spectrometry results for Sb and Br

A comparison between Br and Sb concentrations obtained via X-ray fluorescence with those measured using laser ablation-inductively coupled plasma-mass spectrometry is reported in the SI (Fig. 3 and 4). In summary, Br concentrations detected with X-ray fluorescence showed a strong linear association ($R^2=0.9985$ for Br and $R^2=0.9768$ for Sb) with concentrations detected with laser ablation-inductively coupled plasma-mass spectrometry, validating our X-ray fluorescence method for quantitative analysis of Br and Sb on polymers.

To give an estimation of the BFR concentration equivalent to the detected Br, assuming conservatively that the detected Br

has originated from a widely used BFR with the lowest mass fraction of Br (i.e. triBDE, $\chi_{\text{Br}}=0.59$), Br concentrations above 0.059% w/w would correspond to 0.1 % w/w of BFR (1000 $\text{mg}\cdot\text{kg}^{-1}$), the maximum allowed limit in homogenous material. Of the 26 samples analyzed with X-ray fluorescence, 11 of them (61%) exceeded the estimated low POP concentration limit and 7 more samples exceeded our detection limit ($>0.001\%$ w/w). A quarter of all our samples with detectable concentrations of Br were food-contact articles (Table 3 with Sb and Br concentrations is provided as SI). With the exception of one sample (a blue miniature car launcher from a Dutch distributor), Sb was detected in all samples in which Br was detected. Concentrations of Br spanned between 0.0004 and 1.7% w/w, indicating that BFRs were unintentionally mixed (and their original concentration diluted) via recycling, because if they were intentionally added with the purpose of flame retardancy, they would be present at higher concentrations (10-30% w/w)²².

Compound specific evaluation with thermal desorption-GC-MS

Thermal desorption-GC-MS is a technique that is mainly intended for qualitative evaluation of the compound specific BFR composition of samples. Nonetheless, combining the fully quantitative total elemental information for Br concentration and the inter-sample relative concentration of the detected BFRs, it was possible to obtain compound specific semi-quantitative data

We performed compound specific evaluation on those samples containing Br $> 0.059\%$ w/w (Table 1). With the exception of the single WEEE sample, for which only decaBDE was observed, for all the other 11 samples (toys and food-contact articles) containing $>0.059\%$ w/w Br, PBDEs and TBBP-A were detected together. The most abundant BFR in the majority of cases (73 %) was decaBDE at concentrations ranging from about 200 to about 10000 $\text{mg}\cdot\text{kg}^{-1}$. TBBP-A followed in a range from about 200 to 8000 $\text{mg}\cdot\text{kg}^{-1}$; while BTBPE and DBDPE were detected at trace levels only and not quantified. Although the European Commission moved recently to restrict the use of decaBDE, a low POP concentration limit for this substance has yet to be promulgated. Should a 1000 $\text{mg}\cdot\text{kg}^{-1}$ low POP concentration limit be applied to decaBDE - as it is for the other restricted BDEs - then 45% of the analyzed samples would exceed this limit. No samples exceeded the limits for penta- and octaBDE.

Principal component analysis analysis of the relationship between concentrations of REEs and appliance class

We tested the hypothesis that if circuit boards and other electronic parts (containing REEs and BFRs in high concentrations) are mixed together with polymers, thus leading to contaminated recycled material, then REEs and Br concentrations in items containing such recyclates should vary together. To do so, we conducted principal component analysis of our data on concentrations of individual REEs and Br in our samples. A general evaluation of the principal components was performed analyzing a data table in which the concentrations of Br, Sb, Ca, Ti, Y, La, Ce, Pr, Nd, Sm, Gd,

Tb, Dy were expressed in the same unit for all samples. The first principal component accounted for 68% of the variance where REEs had the highest score in the first component and Br had the highest score in the orthogonal component.²³

Assuming that grouping of REEs is due to their use in different application categories, we grouped the samples by polymer type: polyolefin (PE and PP), styrenic (PS and HIPS) and copolymer (ABS, PC/ABS) before conducting between-group principal component analysis and within-group principal component analysis (data on polymer type were obtained with attenuated total reflection-Fourier transform infrared spectroscopy and pyrolysis GC-MS, for more information see SI, Table 4). In between-group principal component analysis²⁴ data are projected onto the principal components of the group means and this usually leads to a better group separation than in conventional principal component analysis. In within-group principal component analysis, the average within each group is subtracted before the eigenanalysis: this has the effect of detrending a group. After grouping, the variance substantially increased between groups (89.33%) and decreased within groups (60.02%), showing that the polymer type is a valid grouping strategy: when the samples are grouped by polymer, the first component is responsible for ca. 30% more variation in the data. In other terms, the data varies within the same polymer-type to a lesser extent than within all samples, hence the polymer type is responsible for a trend in the data.

Figure 1 shows a biplot of the first two principal components in a matrix of heptaBDE, TBBPA, Br, Sb, decaBDE concentrations for samples of different polymeric matrices. This graphical representation of PCA is called a biplot because it allows row effects (in this case concentration-related variables) and column effects (in this case polymeric matrix-related variables) to be plotted jointly so that factorial axes are represented relative to individual (sample-wise) locations. This type of plot is meaningful when the two chosen components explain the large majority of the variance for the matrix of samples and variables to be represented. In this example this is a valid assumption as 99% of the variance is explained by the first two components (Br and TBBPA). The green lines are called eigenvectors, their length is defined by an eigenvalue. The eigenvalue is the standardized variance i.e. the standard deviation of a certain variable: the longer a vector, the wider the range of values that variable assumes over the sample population. As a rule of thumb, positive and negative correlations between variables can be estimated by the cosine of the angle between their eigenvectors. A more detailed explanation of the theory behind the graphic display of matrices can be found elsewhere.²⁵

The results showed that Br has the highest load in the first component (75%) and TBBPA in the second component (76%). When considering only the ABS based samples, decaBDE has the highest loading in the first component (Fig. 1).

From Fig.2 it is possible to observe how for ABS (group c), Br, Sb and REEs are inter-correlated quantitative dependent

variables. Br, Sb and REEs vectors form a very small angle with each other showing a strong positive correlation, and are almost orthogonal to Ca (no correlation); for HIPS/PS (group b) the Br and Sb vectors have very similar eigenvalues, meaning these variables have a similar influence on the data variance, but REEs eigenvectors are close to zero; for PE/PP (group a) the opposite behaviour is observable, most REEs have similar eigenvectors (which causes them to point in the same direction) and similar eigenvalues (which gives their vectors similar lengths), whereas Br and Sb vectors are instead close to zero, indicating a small influence in the data variation. Martinho et al¹⁰ conducted a study on more than 3000 plastic samples arranging the polymer distribution by appliance class. The following observations are based on their findings: ABS is mainly used for central processing units and small copying equipment, therefore the interdependence of REEs and Br concentrations is explainable with the incorporation of printed circuit boards that contain the central processing units of computers (with high REEs and BFRs content) into the recycle material. The main use of HIPS/PS is in housing for large cooling appliances and TVs. For these larger appliances it is reasonable to assume that separation of the cover from the electric and electronic components is more widely achieved given the dimensions of the parts and the fact that the plastic/circuitry ratio is higher than for small appliances. For these reasons Br and REEs concentrations are not the main factor in the data variation within this polymer group. Finally, in the Guidance for the inventory of PBDEs listed under the Stockholm Convention on POPs (2011) it is reported that BFRs have only a minor use in polyolefins and usually in fibres, not in hard plastic items (such as those analyzed in this study), which explains the low Br and Sb concentrations found for this class of polymers. It was also observed that Ca was in all cases not following the distribution of the other vectors, which is probably because Ca is also added after recycling -when recycled polymers are added to new polymers- in the form of CaCO₃ as an inert filler to facilitate moulding of new large parts, therefore the cause of its increased concentration is not interdependent with REEs concentrations as it happens during a separate process. We thus normalized our data by Ca and analyzed the loadings of each analyte for the first component. For (a) PE/PP the major loading is on Y (used as a catalyst in ethane polymerization) and Nb (used for the production of magnets employed in mobile phones, microphones, loud speakers and headphones), fitting well with the main application of this polymer which is small WEEE. For (b) the major loading is on Ce (used in flat-screen TV and self cleaning ovens) and on Gd (used for cathode ray tube screens), consistent with the main use of HIPS/PS in large appliances and TV sets.¹⁰ The main loading for ABS was on Gd which is also used for data storage disks and central processing units, for which ABS is widely used as casing material. The clustering over polymer type can be explained as follows: different polymers are used for different purposes (depending on the required cost, mechanical resistance, flexibility etc...),

therefore showing different BFRs' types and loadings and will be differently sorted during the recycling rounds. In conclusion, goods that are made of the same polymer type tend to have similar POP profiles because of their similar manufacturing, use and recycling processes.

Future developments

In order to reduce the total BFR content (and thereby cost) while maintaining the same flame retardant effect, a less expensive inorganic flame retardant, Sb_2O_3 , is usually added in a 1:3 ratio with PBDEs. In our study, fluctuations between different samples were noticed in the Sb/Br ratio; which led us to hypothesize that this ratio could be used when performing *in situ* X-ray fluorescence analysis to identify the specific presence of PBDEs as opposed to other non-regulated BFRs such as TBBP-A for which low POP concentration limits do not apply.

Because Sb is used as a co-synergist only with restricted BFRs (i.e. PBDEs), if Br is found in the absence of Sb, the sample is likely to contain a different –non restricted- BFR (e.g. TBBP-A). It is important however to note that detection of Br and Sb in the same sample, does not exclude the presence of TBBP-A. This is because many plastic goods contain recycle from more than one source, whereby PBDEs (and Sb) may be present in one and TBBP-A (without Sb) in another. In such mixed source samples, the deviation from the mass ratio between Br and Sb (~3:1, depending on the exact PBDE formulation present) is a potential metric for the relative amounts of PBDEs and TBBP-A. A study that focuses on the relationship between this ratio and the presence/absence of PBDEs in polymers may provide compound-specific information using hand-held X-ray fluorescence spectrometers.

Conclusions

This study uses X-ray fluorescence for measuring the concentrations of Br and Sb in toys and food-contact articles as an inexpensive, rapid, *in situ* metric for unintentional BFR contamination. Laser ablation-inductively coupled plasma-mass spectrometry measurements on the same samples validates the use of X-ray fluorescence in this application for accurate Br and Sb quantification in polymers. Our results show that – in contravention of Regulation (EC) No. 202/2014-food-contact articles that can be bought on the European market are not being produced exclusively with food-grade polymers, specifically, one third of the food-contact articles in this study tested positive for Br. Compared to food-contact articles, BFRs were more frequently found in children's toys with concentrations in almost half of the samples analysed here exceeding the low POP concentration limits applied for WEEE. Children's toys do not fall under European Commission directives relating to BFRs or REACH unless they have electrical or electronic components, in which case they fall under the WEEE directive. Considering the extent of contact and the

vulnerability to toxic chemicals of their users, this class of consumer goods should undergo the same strict regulation as food-contact articles, banning the use of uncontrolled recycled material at the material sourcing stage.

Our results also provide insights into likely causes of BFR contamination of recycled polymers, specifically poor sorting practices such as laborious sorting of small WEEE and separation of covers from central processing units in small appliances. The identification of the critical points along the waste cycle is the first step for establishing good recycling practices.

Acknowledgements

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/under REA grant agreement No 606857 (ELUTE).

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Sample	decaBDE (mg·kg ⁻¹)	+/-	TBBPA (mg·kg ⁻¹)	+/-	heptaBDE (mg·kg ⁻¹)	+/-
Rubik's cube	328.1	5.2	386.8	5.2	<LOD ^a	-
Toy gun	4352.7	219.6	661.3	219.7	<LOD	-
Spring car	1303.8	66.2	774.4	66.2	<LOD	-
Spring car	944.4	100.4	278.1	94.3	20.0	6.12
Car launcher	9225.8	1143.9	7747.1	1143.9	<LOD	-
Miniature car	284.3	1.9	927.2	1.9	<LOD	-
Miniature car	1279.8	45.3	208.4	47.6	19.1	2.4
Spring gun	210.5	2.8	513.9	2.8	<LOD	-
Thermal Cup	778.8	91.7	442.8	91.7	<LOD	-
Thermal Cup	775.2	16.6	471.3	16.6	<LOD	-
Radio back panel	5118.8	120.5	<LOD	-	<LOD	-

Table 1: Compound specific semi quantitative report of Br-positive samples obtained with TD-GC-MS. The relative concentration of each BFR in each sample was normalized by the total elemental Br measured with XRF. The analytical error is calculated as the SD between duplicate measurements with TD-GC-MS. ^aLOD for heptaBDE is 1 mg/kg⁻¹

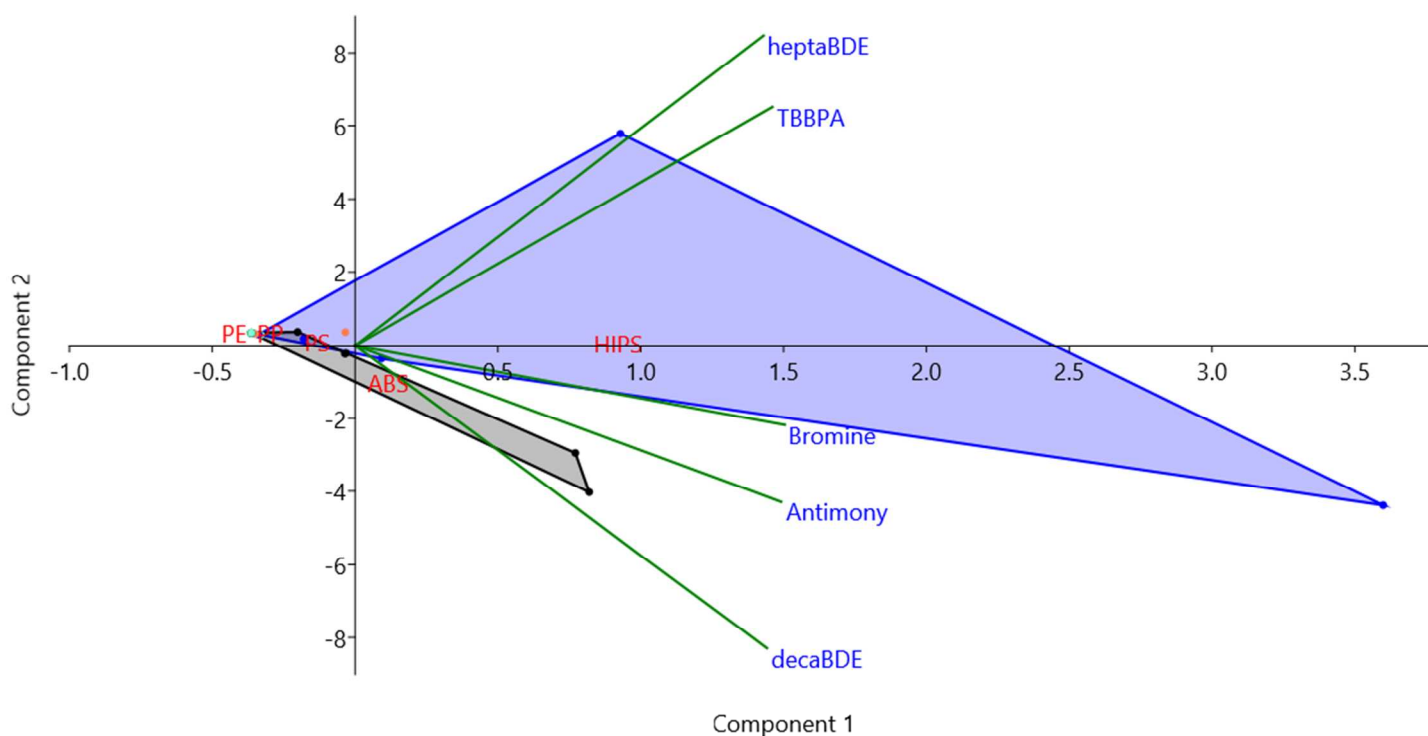
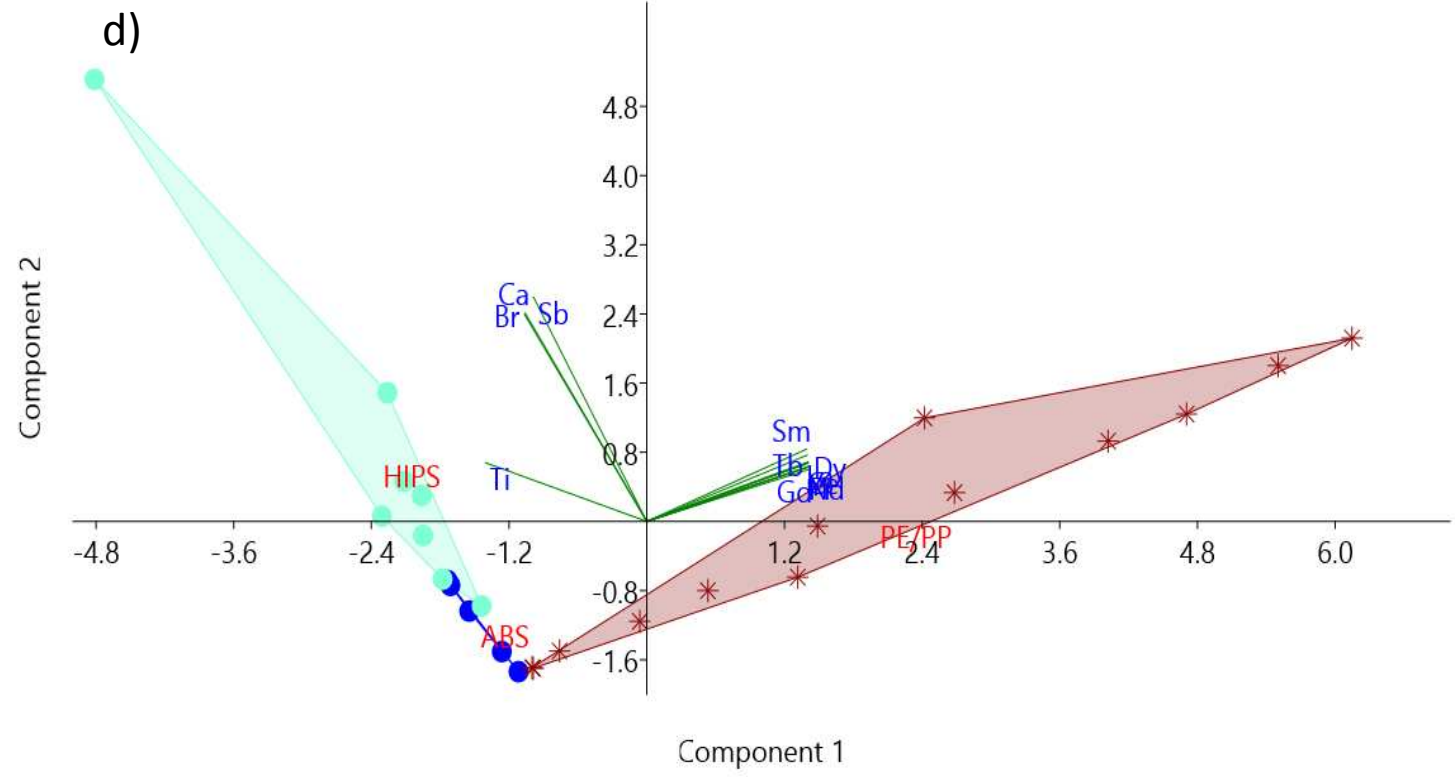
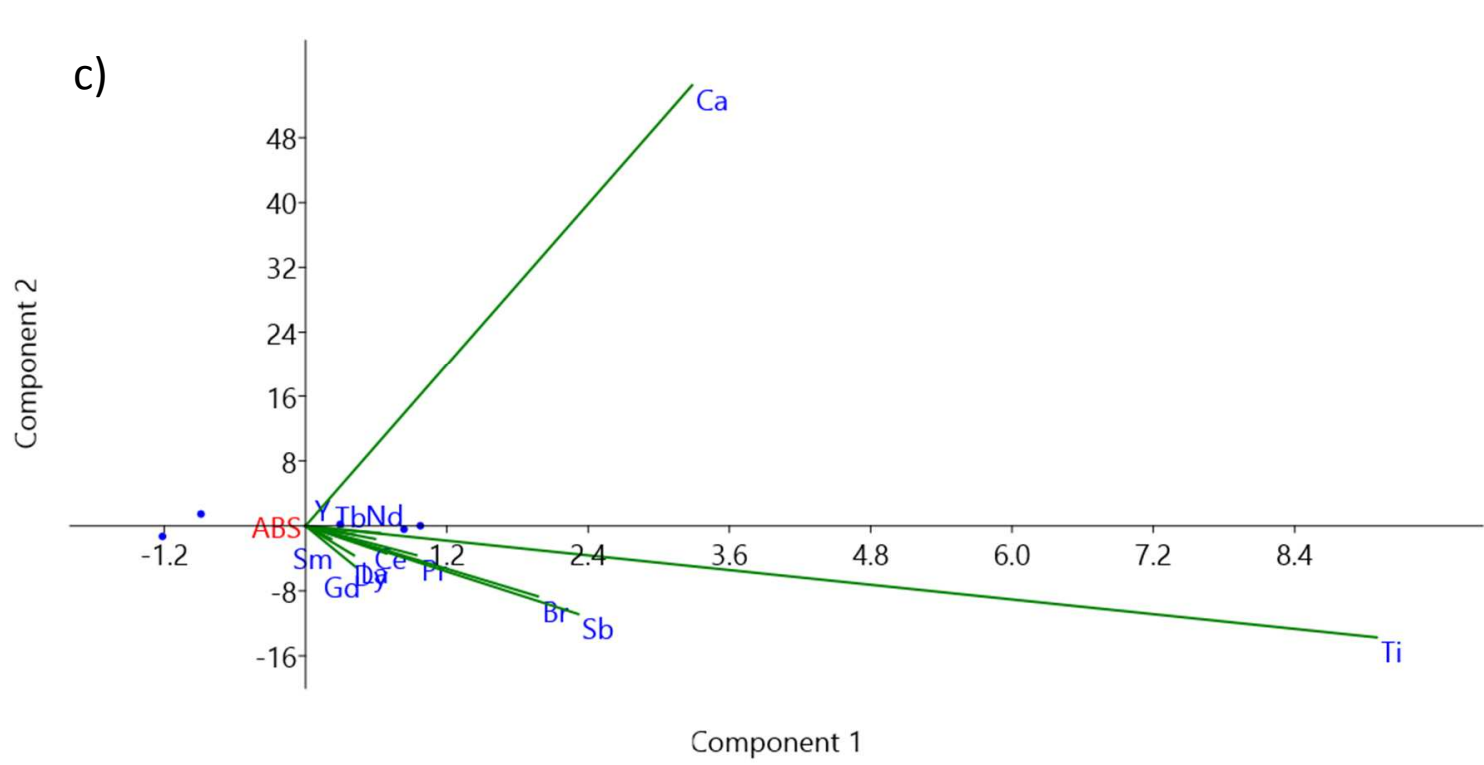
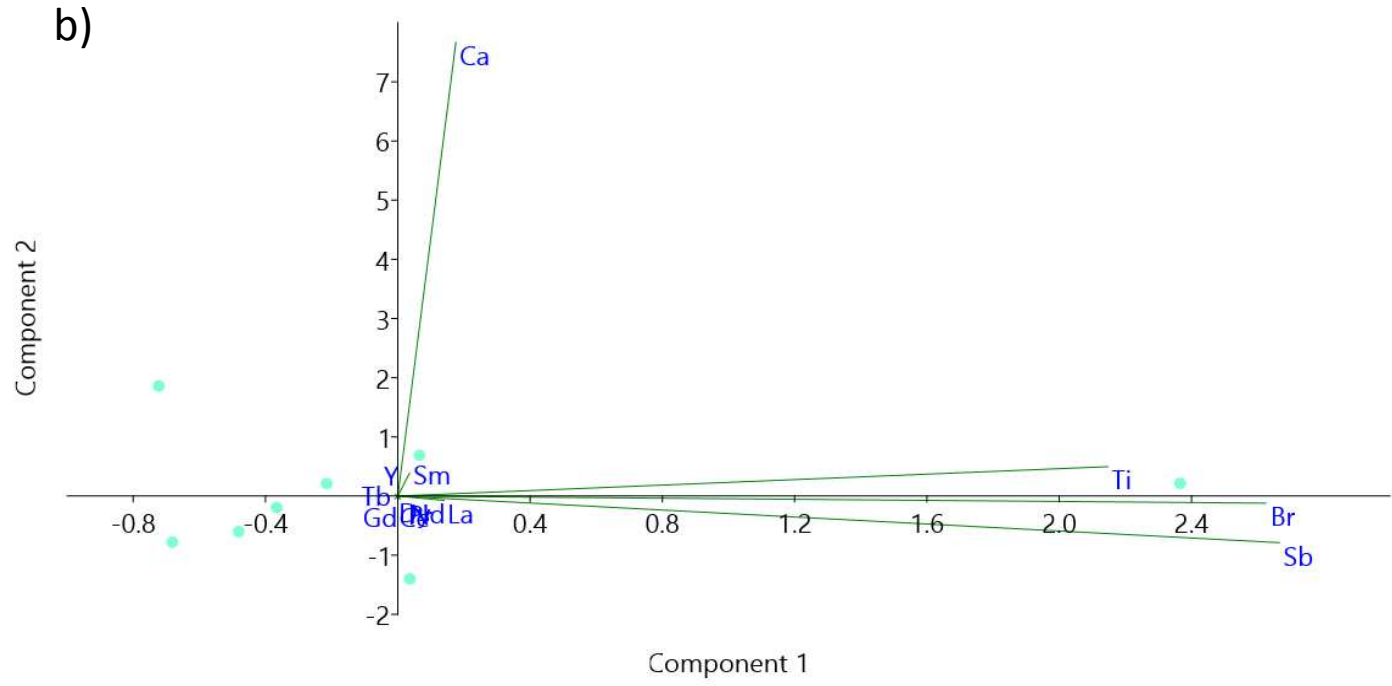
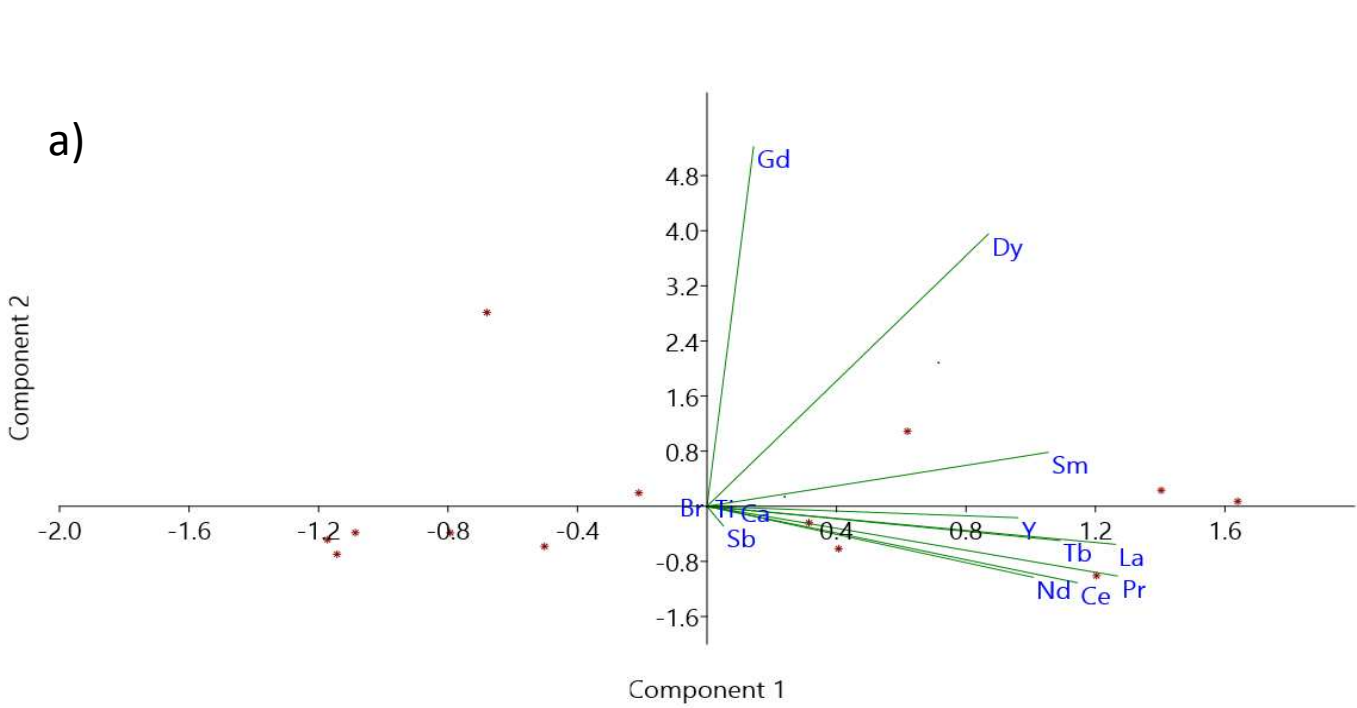


Figure 1 PCA of polymer type and BFR class shown in a biplot of the first two principal components. The angle between vectors shows that concentrations of PBDEs, bromine and antimony are all positively correlated with each other. HIPS samples have the largest positive variations over bromine and TBBPA. ABS samples have smaller but positive variations over antimony, bromine and decaBDE. PP and PE have no noticeable deviations over any of the plotted variables. This is because the concentrations of the above compounds are seen to be the lowest in the PP/PE group of samples.



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Figure 2 Principal Component Analysis for REEs, Br, Sb and inert fillers (Ca and Ti). d) bi-plot of the two main components (Br and Sb accounting for most of the first component and REEs equally accounting for most of the second) for the complete group of samples , the filled colored regions are correlation polygons joining samples groups (grouping is by polymer type). Inspection of the “group” vectors (here represented as aqua-coloured dots for HIPS, blue dots for ABS and red asterisks for PE/PP), shows these to fall into 3 main clusters (corresponding to the type of polymer of each sample). a) bi-plot for olefin polymers: the Br and Sb vector are –for this group- close to zero (as the samples made of this plastic contained little to no BFRs) but positively correlated to the REEs showing a higher influence in the data variability (longer green vectors), b) bi-plot for styrenic polymers: Br and Sb are by far the main contribution to data variability and have a somewhat positive correlation with REEs; samples are seen to have sizeable negative deviations over the first component (Br) . c) bi-plot for acrylic co-polymers: Ti and Ca are the main components, although the weak correlation with Br and Sb (the angle between them approaches 90 degrees) would suggest separate additions to the analyzed samples. When renormalizing this matrix over Ca, the main components result to be REEs (first component) and Br (second component).

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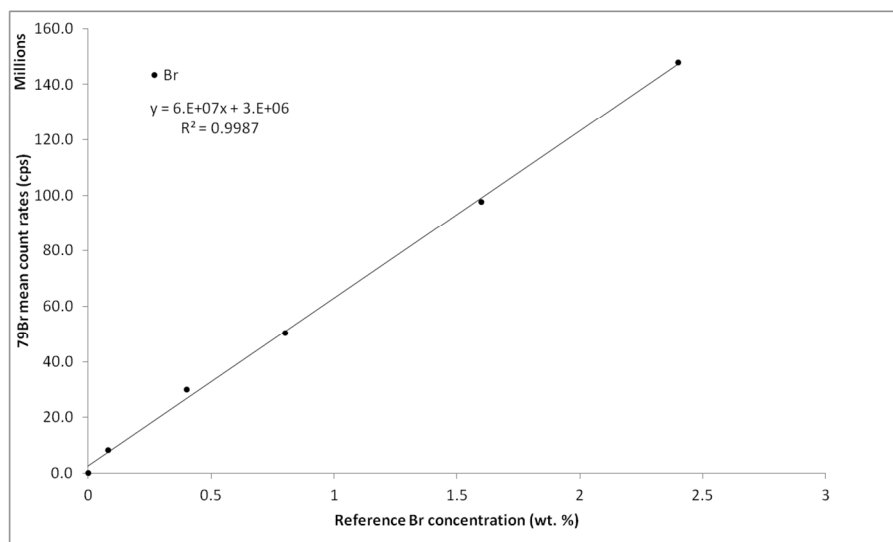
LA-ICP-MS analysis for XRF validation

Figure 1 Calibration curve for ^{79}Br in solid reference material done with LA-ICP-MS. The reference concentration was provided with the reference material's certificate and measured with neutron activation analysis.

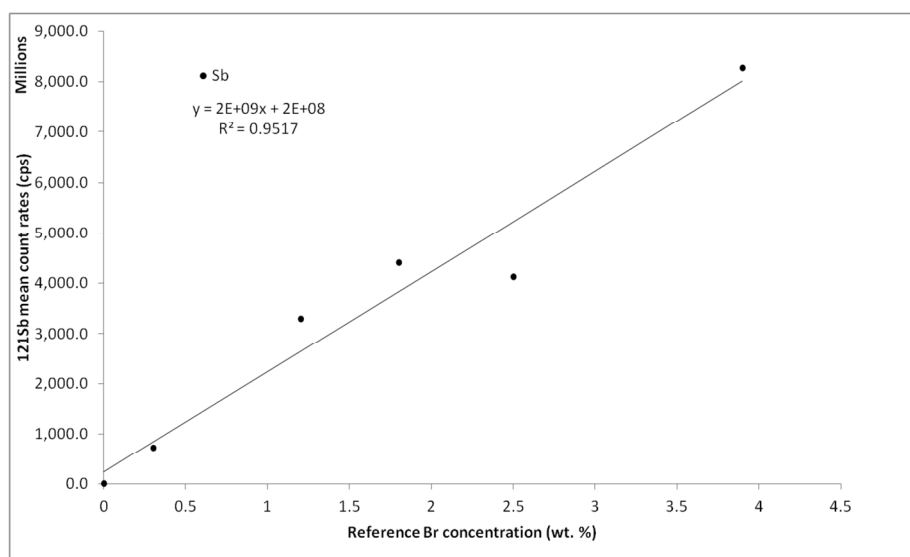


Figure 2 Calibration curve for ^{121}Sb in solid reference material done with LA-ICP-MS. The reference concentration was provided with the reference material's certificate and measured with neutron activation analysis.

For LA-ICP-MS the LOD was 0.0001% of Br and 0.001% of Sb. The average accuracy was 93.3%, with the lowest value of 79%.

For XRF the LOD was 0.001% of Br and 0.0005% of Sb. The average accuracy, calculated comparing the XRF equivalent concentration values and the reference values was 93.9%.

For Br measurements of the calibration standards, the R^2 observed is 0.9985, for the measurements of the real samples instead, when compared to the XRF data, the average relative residual was 11.1%. For Sb the calibration curve shows a slightly worse correlation ($R^2=0.9517$) with the XRF results: this is likely due to the difference in micro-homogeneity (due to different polarities) between Sb_2O_3 and BDE209, which affects the LA-ICP-MS (having a micrometric sampling area) but not XRF (0.8 cm sampling area)¹.

The optimal thermal desorption settings, having the lowest debromination yield for decaBDE209, were: initial temperature 150°C, ramp rate 80°C min⁻¹ to 350°C and held for 2 min. Due to the risk of thermal debromination of PBDEs, an optimal GC interface temperature has been found at 300°C with a high and safe yield for decaBDE-209 and the lowest formation of thermal debromination products (heptaBDEs, octaBDEs and nonaBDEs). At higher temperatures than 310°C, thermal degradation of decaBDE-209 occurs with loss of sensitivity as a consequence.

Pyrolysis and thermal desorption GC-MS methods use the same hardware. After analysis, the sample cup is removed from the furnace by a pressurized shot system and caught in a sample cup-recovery container. The thermal desorption sequence is programmed so that firstly a blank sample cup without any sample or toluene extract is injected and measured in order to evaluate the background of the whole sample path and to screen potential carryover effects from a previous measured sample (sample path and carryover check). As a next step, a sample cup spiked with toluene and quartz wool plugs (without sample) is measured in order to see if there is any contamination from the toluene/quartz wool plug (reference blank measurement) and is then compared with two following measurements of a sample extract/or solid sample (generally performed in duplicate). This 4-position cycle including four measurements is repeated as many times as there are samples. The decision of repeating the measurements twice (instead of 3 times) is due to the fact that these analysis are merely done to confirm the presence of Br in the samples is due to BFRs and subsequently to use their relative content to obtain a semi-quantitative result when combined with total elemental Br quantification. The demonstrated hardware configuration and application has proven its effectiveness and stability in the past and is described elsewhere in more detail²⁻⁶.

Table 1 Composition report of the Inter laboratory TV casing sample used for TD-GC-MS calibration.

Results of TV casing composites (InterLab Sample Waste TV backplate)			
Compounds	<i>n</i>	Mean Conc.	%RSD
PBDEs		($\mu\text{g/g}$)	
2,4,4'-TrBDE (#28)	4	0.024	10
2,2',4,4'-TeBDE (#47)	4	1.3	15
2,2',4,4',5-PeBDE (#99)	4	3.2	27
2,2',4,4',6-PeBDE (#100)	4	1.1	39
2,2',4,4',5,5'-HxBDE (#153)	4	520	26
2,2',4,4',5,6'-HxBDE (#154)	4	59	22
2,2',3,4,4',5,6'-HpBDE (#183)	4	3700	21
2,2',3,3',4,4',5,6'-OBDE(#196)	2	930	--
2,2',3,3',4,4',6,6'-OBDE(#197)	2	2100	--
2,2',3,3',4,4',5,5',6-NoBDE(#206)	2	3000	--
2,2',3,3',4,4',5,6,6'-NoBDE(#207)	2	1950	--
DeBDE (#209)	4	90000	19
TrBDEs	4	0.059	7
TeBDEs	4	1.4	14
PeBDEs	4	5.8	26
HxBDEs	4	620	24
HpBDEs	4	3700	21
OBDEs	4	3000	25
NoBDEs	4	4800	19
Other BFRs		($\mu\text{g/g}$)	
TBBPA	3	6800	11
2,4,6-Tribromophenol (TBP)	3	5	44
HBCD	2	13	--
<i>n</i> : number of analysis			
--: not calculated			

The Inter laboratory TV casing sample was a composite of 50 cathode ray tube (CRT) back casings (high impact polystyrene) that had been melted and remoulded to form a material for interlaboratory tests. The data in this table was part of a recent study ⁷ and obtained analyzing four replicates of the TV casing using methods reported previously ⁸

Table 2 TD-GC-MS method operating ranges

Compound	Method operating range (mg/Kg ⁻¹)
PBDEs (tri- to decaBDE)	1-10000
TBBPA	70-7000
DBDPE	20-10000
BDTPE	90-10000

Table 3 Br and Sb concentrations obtained with XRF. The analytical error is calculated as a function of SD between triplicate measurements

	Manufactured	Purchased	Br%	+/- Br%	Sb %	+/- Sb %
Shield toy	China	Czech Republic	0.01346358	0.002168	0.011346	0.004734
sword toy	China	Czech Republic	0.010814214	0.007282	0.012588	0.007516
Olympics medal toy	China	Czech Republic	0.009899217	0.004288	0.008359	0.005798
Rubik's cube - Czech Republic	China	Czech Republic	0.018397253	0.006736	0.014477	0.004642
Rubik's cube - German	China	Germany	0.071483044	0.001688	0.029365	0.006126
Black Gun toy	China	Germany	0.501407974	0.02219	0.257966	0.015084
Star Wars cereal bowl	China	Germany	<LOD	0.002602	<LOD	0.004134
thermal cup	China	Germany	<LOD	0.008238	<LOD	0.004462
small gun toy	China	Italy	<LOD	0.000392	<LOD	0.004522
binocular toy	China	Italy	<LOD	0.001238	<LOD	0.004694
target man toy	China	Italy	0.002427124	0.000768	<LOD	0.004814
spring gun toy	China	Italy	0.072438773	0.000834	0.037547	0.004422
spring gun red toy	China	Italy	<LOD	0.001326	<LOD	0.006126
black spring car	China	Germany	0.20782717	0.000482	0.089293	0.01027
black spring car	China	Germany	0.124255989	0.000512	0.054242	0.008074
blue car launcher	China	Germany	0.053600627	0.000634	<LOD	0.008182
grey car launcher	China	Germany	1.697292321	0.002308	0.84359	0.005174
grey miniature car	China	Germany	0.121146101	0.000454	0.091256	0.006018
black miniature car	China	Germany	0.150725521	0.000422	0.069648	0.00335
thermal cup	China	Czech Republic	0.002147532	0.000404	0.003619	0.00718
thermal cup	China	Czech Republic	<LOD	0.002672	<LOD	0.004286
thermal cup	China	Czech Republic	0.122153203	0.000352	0.071907	0.00593
thermal cup	China	Czech Republic	<LOD	0.002724	<LOD	0.0043
thermal cup	Turkey	Czech Republic	0.124649681	0.008786	0.073652	0.007874
thermal cup	Turkey	Czech Republic	<LOD	0.000348	<LOD	0.004636
thermal cup	Turkey	Czech Republic	<LOD	0.0003	<LOD	0.004324
Radio back panel	China	Czech Republic	0.511882529	0.00037	0.343974	0.004998

Table 4 Overview of ATR-FTIR and pyrolysis GC-MS data on polymer composition

Sample	Main polymer ^a	Impurities/majors ^b				
		PS/HIPS/ABS/SAN	PC	PMMA	PA6	PET/PBT
Rubik's cube	HIPS	+	+	+	+	+
Toy gun	HIPS	+	+	+	+	+
Spring car	HIPS	+	+	+	n.d.	+
Spring car	HIPS	+	+	+	n.d.	+
Car launcher	HIPS	+	+	n.d.	n.d.	+
Miniature car	PS	+	+	+	n.d.	+
Miniature car	PS	+	+	+	n.d.	+
Spring gun	HIPS	+	+	+	n.d.	+
Thermal Cup	ABS	+	+	+	n.d.	+
Thermal Cup	ABS	+	+	+	n.d.	+
Radio cover	ABS	+	+	+	n.d.	+

^aData obtained by FTIR

^b Data obtained by pyrolysis GC-MS; the symbol "+" means that polymer's specific precursors were detected in the pyrogram while "n.d." means not detected. The polymer precursors in the pyrogram are styrene (PS/HIPS/ABS/SAN); bisphenol A (PC); methylmethacrylate (PMMA); caprolactam (PA6) and benzoic acid (PET/PBT).

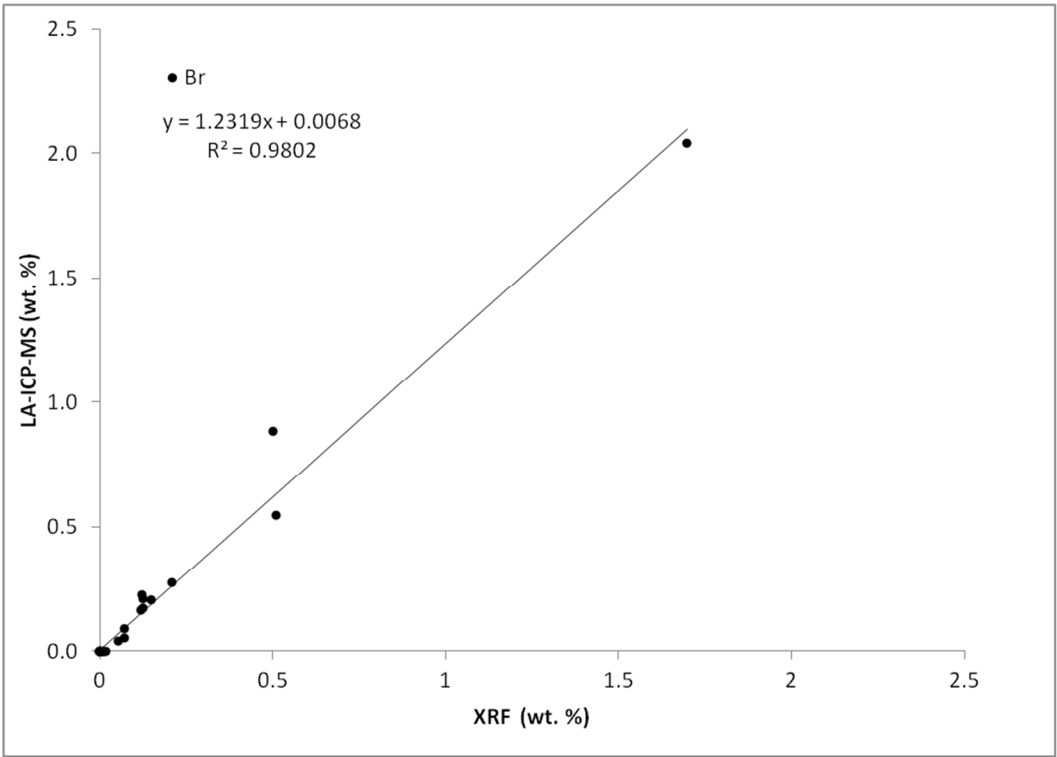
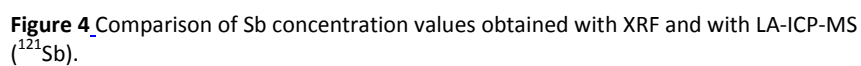


Figure 3 Comparison of Br concentration values obtained with XRF and with LA-ICP-MS (⁷⁹Br).



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